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(54) ABRASIVE CLEANING COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4., England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to abrasive cleaning compositions, particularly to such compositions in powder form which are sometimes called scouring powders and are commonly used for cleaning sinks and the like.

Powdered abrasive cleaning compositions normally incorporate as major ingredients finely divided water-insoluble abrasive materials, with minor amounts of surface active agents, bleaching or disinfecting agents and the like. It is difficult to incorporate into such compositions liquid ingredients which react with the bleaching and disinfecting agents used, for example perfumes. Also it is difficult to incorporate appreciable quantities of liquid without deleteriously affecting the free-flowing properties of the compositions.

According to the present invention a powdered abrasive cleaning composition comprises a water-insoluble abrasive and water-soluble microcapsules of partially-hardened gelatin enclosing an organic liquid ingredient.

The use of partially-hardened gelatin micro-capsules ensures that the micro-capsules are not ruptured to an excessive degree during their processing, transportation or storage, but they are readily broken by abrasive action or rapidly dissolved in use to liberate the encapsulated liquid. The present invention makes it possible to include a perfume, a preferred example of an organic liquid ingredient, in powdered abrasive cleaning compositions without excessive loss by evaporation during storage and use, and without reaction between the perfume and the chlorine bleach ingredients commonly used in such compositions.

As mentioned above, powdered abrasive cleaning compositions incorporate as major ingredients finely divided water-insoluble abrasive materials. These materials are usually siliceous abrasives, and include for example felspar, quartz, pumice, bentonite, talc, silica, calcite, alumina, zirconium silicate, diatomaceous earth, china clay, and mixtures thereof. It is desirable that the abrasive material should have a very small particle size, preferably not greater than about 100 microns for the maximum particle size, with the bulk of the abrasive material preferably having a particle size below about 50 microns. The amount of the abrasive material in the abrasive cleaning compositions is generally between about 60% and about 98%, preferably within the range of from about 80% to 95%, by weight of the composition.

It is normal to incorporate in the abrasive cleaning compositions an amount of a water-soluble organic surface active agent, which may be anionic, cationic, amphoteric, zwitterionic or nonionic in character, provided that it is compatible with the other ingredients in the compositions. The usual surface active agents are materials with detergent active properties which are relatively cheap and readily available, particularly the anionic detergent active compounds such as soaps and sulphated or sulphonated synthetic detergent active compounds, particularly those which contain from 8 to 24 carbon atoms per molecule. Particular anionic detergent active compounds which may be mentioned are alkyl sulphates, alkyl benzene sulphonates, alkyl ether sulphates and olefin sulphonates, by which latter term is meant the products of sulphonation of olefins with sulphur trioxide followed by neutralisation and hydrolysis. Nonionic detergent active compounds which may be used alternatively, include for example polyethylene oxide condensation products with alkyl phenols and higher aliphatic alcohols. The amount of

organic detergent active compound used is generally in the range of from about 0.5% to 15%, preferably from about 1 to 5% by weight of the compositions.

It is also common practice to incorporate in abrasive cleaning compositions amounts of bleaching agents, particularly chlorine-liberating materials which are obtainable in powder form. Alternatively, oxygen-liberating bleaching agents can be used but they tend to have a less effective disinfecting action, which is particularly valuable in the cleansing of domestic sinks and other surfaces where food is prepared. The preferred organic chlorine bleach ingredients are N-chloro compounds, such as dichloroisocyanuric acid and trichloroisocyanuric acid and salts such as sodium and potassium dichloroisocyanurates. Other N - chloro - imides which can be used include N-chlorosuccinimide and N-chlorophthalimide, and derivatives of dialkyl hydantoin such as 1,3 - dichloro - 5,5 - dimethyl hydantoin, 1,3 - dichloro - 5 - methyl - 5 - ethyl hydantoin and 1,3 - dichloro - 5,5 - diisobutyl hydantoin. Inorganic chlorine bleach ingredients include, for example, lithium hypochlorite, calcium hypochlorite tetrahydrate and chlorinated trisodium phosphate. Oxygen-liberating bleaching agents include for example sodium perborate and sodium percarbonate.

The amount of any bleaching agent used is generally from about 0.1 to 20% by weight of the composition, preferably from about 0.5 to 5% by weight. In the case of chlorine-liberating bleaches, the amount of available chlorine is generally in the range of from about 0.05 to 5%, preferably about 0.2 to 2% chlorine. If desired, the bleaching agent may be coated to preserve to a greater extent the chlorine or oxygen-liberating capacity of the material during storage. In this case the coating material should preferably be water-soluble to facilitate rapid and complete liberation of the active bleaching agent when the composition is used.

Further information on suitable abrasive materials, surface active agents and bleaching agents for abrasive cleaning compositions is readily available in the technical literature.

The ingredients may be encapsulated in partially-hardened gelatin using conventional chemical or physical micro-encapsulation techniques. In the case of the liquid ingredients, micro-encapsulation processes based on the principle of coacervation are preferably used. In such processes the liquid ingredient is finely dispersed in an aqueous medium from which gelatin is deposited on the fine liquid droplets to form embryonic capsules, after which the gelatin coating is hardened or gelled. The capsules formed are then separated from the aqueous medium and dried. The amount of liquid in the capsules may be as high as about 90% or even more by weight but such capsules tend to be too fragile for normal use. It is preferred to use capsules with thicker walls so that not more than about 80% by weight is liquid, for example from about 20 to 75% by weight of liquid, depending on the capsule size, as the proportion of liquid present may be increased in the larger micro-capsules whilst retaining a uniform gelatin wall thickness.

Partial hardening of the gelatin capsules as desired, is preferably accomplished by cross-linking the gelatin molecules, which strengthens the gelatin wall. This is accompanied by decreased water-solubility of the gelatin, but the degree of hardening adopted should not be such as to render the gelatin capsules insoluble in domestic cold water. It is desired that a high proportion of the micro-capsules should rupture during use, either by abrasive action or by solubilisation in water within a short period of not more than about 30 seconds. Hardening may be effected by contacting the gelatin micro-capsules with an aldehyde, usually a lower alkyl mono- or di-aldehyde, for example formaldehyde and glutaraldehyde.

Other known methods of hardening gelatin capsules include for example, treatment with aromatic or aliphatic hardening agents, such as epoxy-type compounds, resin hardeners, mineral hardeners, salting-out agents and gelatin modifying agents.

The gelatin micro-capsules preferably have a size similar to that of the particles of the abrasive cleaning composition in which they are used, that is up to about 100 microns in diameter, but they may be up to about 300 microns in diameter.

It will be appreciated that for the coacervation process of micro-encapsulation, it is necessary for the liquid ingredient to be organic in nature. The liquid ingredient is usually a perfume.

Any perfume used in the partially-hardened gelatin micro-capsules will normally be selected so as to have an odour which is compatible with any chlorine odour which may otherwise be apparent during use of the compositions. It is, however, advantageous that the perfume ingredients need not be chosen individually so as to be completely stable to chlorine, because the micro-encapsulation of the perfume keeps it separate from any chlorine-liberating agent present in the composition until the time of use.

The amount of perfume used is normally from about 0.05 to 3%, preferably from about 0.1 to 1% by weight of the composition. Thus if only about 50% by weight of the micro-capsules is perfume, the amount of the micro-encapsulated perfume in an abrasive cleaning composition would normally be from about 0.1% to 6% by weight, preferably from about 0.2 to 2% by weight, in this instance.

The abrasive cleaning compositions of the invention may additionally comprise a perfume not in micro-encapsulated form, and this may have an odour distinct from that of a perfume in micro-encapsulated form.

The abrasive cleaning compositions of the invention may include any of the usual additives to compositions of this type, for example inorganic fillers or builders such as alkali metal silicates, chlorides, carbonates, sulphates and phosphates. Alkaline salts such as trisodium orthophosphate are particularly useful. Other optional ingredients include organic sequestrants such as nitrilotriacetic and ethylene diamine tetraacetic acid and salts thereof, sodium carboxymethylcellulose, optical brighteners, anti-caking agents and whiteners. It has also been proposed to include in abrasive cleaning compositions colourants, particularly pigments, which lose their colour or change colour by reaction with another ingredient of the composition, usually a chlorine-bleaching agent, when the composition is used.

The invention is illustrated by the following Examples in which parts and percentages are by weight except where otherwise indicated.

Example 1

An abrasive cleaning composition was made by conventional techniques, and 6% of perfume GS66 supplied by Proprietary Perfumes Ltd, in water-soluble partially-hardened gelatin micro-capsules, was admixed with the composition using a Rotacube mixer. The micro-capsules had an average size of 20 microns and contained 45 to 50% of perfume. Samples of the powdered composition were extracted from the mixer after 20, 60 and 180 minutes and the proportion of capsules ruptured in the mixing process were ascertained. A similar procedure was also followed with a composition made using unhardened gelatin micro-capsules of perfume. The formulation of the compositions were as shown below:

Ingredient	Percentage
felspar powder (less than 100 microns)	84.2
sodium dodecyl benzene sulphonate	3.7
trisodium orthophosphate	5.0
colourant and moisture	0.1
trichloroisocyanuric acid	0.5
sodium sulphate	0.5
micro-encapsulated perfume	6.0
	100.0

The test results are given below:

Mixing Time (mins)	Percentage Capsule Rupture: Partially Hardened Gelatin	Unhardened Gelatin
0	2.6	8.7
20	7.3	13.9
60	10.6	17.9
180	13.0	22.6

These figures show the benefit of using partially hardened gelatin capsules in terms of decreased capsule rupture in processing, although it will be appreciated that the longer mixing times were particularly severe and would normally be avoided if possible.

Example 2

A series of abrasive cleaning compositions were prepared incorporating about 0.5% perfume PRE 107 from Proprietary Perfumes Ltd in gelatin micro-capsules. The capsules contained about 45—50% by weight of perfume and had an average diameter of about 20 microns and were either unhardened or hardened by incorporating 0.5, 1.0, 1.5 or 2.0% glutaraldehyde in the gelatin. A further composition was made using perfume PRE 107 in insoluble urea-formaldehyde micro-capsules.

The compositions had the following formulation:

Ingredient	Percentage
felspar powder	92.4
sodium dodecyl benzene sulphonate	1.8
sodium sulphate	0.5
trisodium orthophosphate	3.6
trichloroisocyanuric acid	1.0
colourant and moisture	0.2
encapsulated perfume	0.5
	100.0

The compositions were used for simulated domestic sink scouring and the quality of the odours of the perfumes assessed by experienced assessors. The odour of the compositions with unhardened gelatin encapsulated perfume was found to be modified and less pleasant than that produced by the compositions with partially-hardened gelatin capsules. The odour from the composition having urea-formaldehyde capsules was satisfactory but noticeably weaker than that from the compositions of the invention.

Example 3

An abrasive cleaning composition was made using 0.5% of perfume GS66 encapsulated in partially hardened gelatin micro-capsules

containing 45—50% of perfume. The capsules had an average diameter of about 20 microns and were hardened with 1.5% glutaraldehyde based on the gelatin.

The composition had the following formulation and was found to have excellent properties for retention and stability of perfume odour in storage:

Ingredient	Percentage
calcite powder	90.3
sodium dodecyl benzene sulphonate	4.0
sodium tripolyphosphate	2.0
sodium sulphate	1.0
sodium metasilicate	0.2
sodium perborate	1.0
sodium carbonate	1.0
encapsulated perfume	0.5
	100.0

Examples 4 to 6

Four abrasive cleaning compositions were prepared with the following base formulation:

Ingredient	%
calcite powder	93.4
sodium alkyl benzene sulphonate	4.0
sodium tripolyphosphate	0.9
trichloroisocyanuric acid	0.6
water+salts	1.1

To this base formulation were added various amounts of perfumes in encapsulated or unencapsulated forms as follows:

Example	Perfume
4	0.2% of perfume GS66 and 0.1% of micro-encapsulated perfume GS66
5	0.2% of perfume GS66 and 0.15% of micro-encapsulated perfume GS88
6	0.6% of micro-encapsulated perfume GS66

All the micro-capsules were formed of gelatin hardened with 1.5% of glutaraldehyde and contained 7% by weight of the capsules of Sandoz acid green dye in the gelatin wall.

These compositions were tested for their colour effect and odour after storage for 3 months at various conditions of temperature and humidity and the results were as follows:

TABLE I

Example	Storage Conditions	Variation In: Colour	Odour
4	2°C	None	None
"	Ambient	None	None
"	37°C	None	Slight
"	37°C/70% RH	None	Slight
5	2°C	None	None
"	Ambient	None	None
"	37°C	None	Very Slight
"	37°C/70% RH	None	Slight
6	2°C	None	None
"	Ambient	None	Very Slight
"	37°C	None	Slight
"	37°C/70% RH	None	Slight

These results indicate that the perfume capsules had excellent colour stability, and that only under severe storage conditions did any significant variation of the perfume odour occur.

Examples 7 to 10

Four samples of water-soluble gelatin capsules incorporating perfume supplied by Proprietary Perfumes Ltd, wherein the capsule walls incorporated different levels of glutaraldehyde as a partial hardening agent, were added at a level of 6% to a conventional abrasive cleaning composition. The composition was then subjected to various mechanical treatments and the extent to which the capsules were ruptured by these treatments was determined.

The amounts of glutaraldehyde in the capsule walls were as follows:

Example	% of glutaraldehyde
7	0.5
8	1.0
9	1.5
10	2.0

The formulation of the abrasive cleaning compositions incorporating the capsules, was:

Ingredient	Percentage
Sodium alkyl benzene sulphonate	2.5
Trisodium orthophosphate	3.6
Trichloroisocyanuric acid	1.0
Encapsulated perfume	6.0
Felspar	to 100

The various mechanical treatments used, and their effects on the capsules, are given in Table II below:

TABLE II

Treatment	Example	% of capsules ruptured 7	8	9	10
None (capsules as supplied)		7.9	4.3	4.3	4.1
Incorporation into the composition and mixing for 20 minutes in Rotacube mixer.		13.2	5.1	5.4	7.1
Incorporation into the composition and mixing for 1 hour in Rotacube mixer.		12.7	5.9	6.9	9.4
Incorporation into the composition and mixing for 20 minutes in ball mill		28.7	24.2	28.3	30.7

The above results indicate that the bulk of the partially hardened capsules can withstand severe processing conditions without being ruptured. The capsules of Examples 8 and 9, incorporating 1.0% and 1.5% of glutaraldehyde respectively, in the gelatin capsule walls, were particularly successful.

WHAT WE CLAIM IS:—

1. A powdered abrasive cleaning composition comprising a water-insoluble abrasive and water-soluble microcapsules of partially-hardened gelatin enclosing an organic liquid ingredient.

2. A composition according to claim 1 wherein the encapsulated organic liquid ingredient is a perfume.

3. A composition according to claim 2 wherein the organic liquid ingredient comprises from about 0.05% to 3% by weight of the composition.

4. A composition according to claim 3 wherein the organic liquid ingredient comprises from about 0.1% to 1% by weight of the composition.

5. A composition according to any of the preceding claims wherein not more than about 80% by weight of the capsules is liquid ingredient.

6. A composition according to claim 5 wherein from about 20% to 75% by weight of the capsules is liquid ingredient.

7. A composition according to any of the preceding claims comprising from about 60% to about 98% by weight of finely divided abrasive material.

8. A composition according to any of the preceding claims comprising from about 0.5% to 15% of a water-soluble organic surface active agent.

9. A composition according to any of the preceding claims comprising from about 0.1% to 20% of a bleaching agent.

10. A composition according to claim 9 wherein the bleaching agent is a chlorine liberating bleaching agent.

11. A composition according to any of the preceding claims wherein the gelatin microcapsules are partially-hardened with an aldehyde.

12. A composition according to claim 11 wherein the amount of aldehyde used is from 0.5% to 2.0% of glutaraldehyde on the weight of the capsules.

13. A composition according to any of the preceding claims additionally comprising a perfume not in micro-encapsulated form.

14. A composition according to claim 13 wherein the additional perfume has an odour distinct from that of a perfume in micro-encapsulated form.

15. A composition according to any of the preceding claims substantially as described herein with reference to any of the foregoing Examples.

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